He atom and other atoms with more than two electrons
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1. Hamiltonian of He atom

The nucleus of a He atom consists of two protons and two electrons. There are two electrons in orbit around the nucleus. Here we neglect the motion of the nucleus, assuming it to be infinitely heavy. An idealized classical picture of the system is shown below.
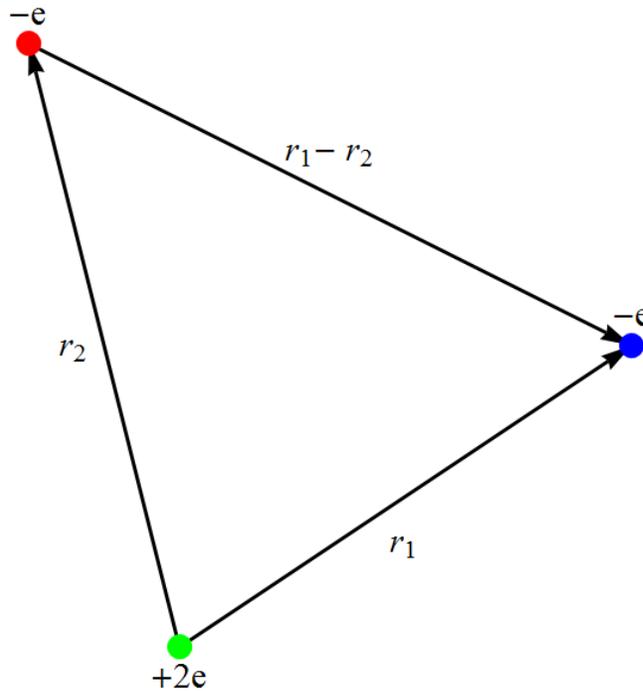

Fig. Co-ordinates used in the formation of the Helium Hamiltonian

The Hamiltonian of He atom, in a frame where the nucleus is at rest, is given by

$$\hat{H} = \frac{1}{2m_e}(\hat{p}_1^{\;2} + \hat{p}_2^{\;2}) - \frac{2e^2}{|\hat{r}_1|} - \frac{2e^2}{|\hat{r}_2|} + \frac{e^2}{|\hat{r}_1 - \hat{r}_2|},$$

where $e>0$, m_e is the mass of electron, $\hat{r}_1$ and $\hat{r}_2$ are the position operators of the two electrons. There are attractive Coulomb interactions between protons ($2e$) and electron ($-e$), and repulsive Coulomb interaction between two electrons. This Hamiltonian is separated into two parts; the unperturbed Hamiltonian as

$$\hat{H}_0 = \hat{H}_{01} + \hat{H}_{02} = (\frac{1}{2m_e}\hat{p}_1^{\;2} - \frac{2e^2}{|\hat{r}_1|}) + (\frac{1}{2m_e}\hat{p}_2^{\;2} - \frac{2e^2}{|\hat{r}_2|}),$$

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and the perturbation Hamiltonian as

$$\hat{H}_1 = \frac{e^2}{\left|\hat{\boldsymbol{r}}_1 - \hat{\boldsymbol{r}}_2\right|}.$$

We note that both $\hat{H}_0$ and $\hat{H}_1$ are independent of spins.

2. Simultaneous eigenstate of $\hat{H}_0$, $\hat{P}_{12}{}^{space}$, and $\hat{P}_{12}{}^{spin}$

Because $\hat{H}_0$ contains no interaction between the individual electrons, it represents a Hamiltonian of two isolated electrons, each under the influence the same nucleus. The Hamiltonian $\hat{H}_0$ does not contain the spin operators. The Schrödinger equation is satisfied by each component of the wave function; in other words, the wave function of the system can be expressed in the form of a product,

$$\left|\psi\right\rangle = \left|\phi^{space}\right\rangle \otimes \left|\chi^{spin}\right\rangle.$$

Note that the Schrödinger equation essentially determines only the space function $\left|\phi^{space}\right\rangle$, the spin function $\left|\chi^{spin}\right\rangle$ remaining arbitrary. The exchange operator can be expressed by

$$\hat{P}_{12} = \hat{P}_{12}{}^{space}\hat{P}_{12}{}^{spin},$$

where the operator $\hat{P}_{12}{}^{spin}$ inter-exchanges the spin states of the two electrons and $\hat{P}_{12}{}^{space}$ inter-exchanges the position coordinate. We have the commutation relations,

$$[\hat{H}_0, \hat{P}_{12}{}^{space}] = 0, \qquad [\hat{H}_0, \hat{P}_{12}{}^{spin}] = 0, \qquad [\hat{P}_{12}{}^{space}, \hat{P}_{12}{}^{spin}] = 0.$$

So we can find the simultaneous eigenket of $\hat{H}_0$, $\hat{P}_{12}{}^{space}$, and $\hat{P}_{12}{}^{spin}$,

$$\left|\psi\right\rangle = \left|\phi^{space}\right\rangle \otimes \left|\chi^{spin}\right\rangle,$$

such that

$$\hat{P}_{12}{}^{spin}\left|\chi^{spin}\right\rangle = \pm\left|\chi^{spin}\right\rangle, \qquad \hat{P}_{12}{}^{space}\left|\phi^{space}\right\rangle = \pm\left|\phi^{space}\right\rangle,$$

$$\hat{H}_0\left|\psi\right\rangle = E_0\left|\psi\right\rangle$$

Note that

$$(\hat{P}_{12}{}^{spin})^2 = (\hat{P}_{12}{}^{space})^2 = \hat{1}$$

We have

$$\hat{P}_{12}{}^{space} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \hat{\sigma}_x$$

The eigenket $\hat{P}_{12}{}^{space}$ for the eigenvalue +1 is

$$\left| \phi_s{}^{space} \right\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}. \qquad \text{(symmetric)}$$

The eigenket $\hat{P}_{12}{}^{space}$ for the eigenvalue -1 is

$$\left| \phi_a{}^{space} \right\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}. \qquad \text{(anti-symmetric)}$$

$\hat{P}_{12}{}^{spin}$ is the Dirac exchange operator and is defined by

$$\hat{P}_{12}{}^{spin} = \frac{1}{2}(\hat{1} + \hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2).$$

We note that

$$\hat{P}_{12}{}^{spin} \left| ++ \right\rangle = \left| ++ \right\rangle \qquad (\left| ++ \right\rangle \text{ is the eigenket of } \hat{P}_{12}{}^{spin} \text{ with eigenvalue +1}).$$

$$\hat{P}_{12}{}^{spin} \left| -- \right\rangle = \left| -- \right\rangle \qquad (\left| -- \right\rangle \text{ is the eigenket of } \hat{P}_{12}{}^{spin} \text{ with eigenvalue +1}).$$

Since

$$\hat{P}_{12}{}^{spin} \left| + - \right\rangle = \left| - + \right\rangle$$

$$\hat{P}_{12}{}^{spin} \left| - + \right\rangle = \left| + - \right\rangle$$

under the basis of $\left| + - \right\rangle$ and $\left| - + \right\rangle$, $\hat{P}_{12}{}^{spin}$ can be expressed as

$$\hat{P}_{12}{}^{spin} = \hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

The eigenket of $\hat{P}_{12}^{\,spin} = \hat{\sigma}_x$ is given by

$$\frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle) \qquad \text{for the eigenvalue } (+1),$$

and

$$\frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle) \qquad \text{for the eigenvalue } (-1).$$

In summary, the eigenket of $\hat{P}_{12}^{\,spin}$ for the eigenvalue $(+1)$ is

$$\left| \chi_s^{\,spin} \right\rangle = \begin{cases} |++\rangle \\ \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle) \\ |--\rangle \end{cases}. \quad \text{(symmetric)}$$

The eigenket of $\hat{P}_{12}^{\,spin}$ for the eigenvalue (-1) is

$$\left| \chi_a^{\,spin} \right\rangle = \frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle). \quad \text{(anti-symmetyric)}$$

3. Commutation relations for the total orbital and spin angular momentum

We consider the Hamiltonian

$$\hat{H} = \hat{H}_{01} + \hat{H}_{02} + \hat{H}_1$$

Note that $\hat{H}_{01}$, $\hat{H}_{02}$, and $\hat{H}_1$ are central fields, where the interactions depends only on the distances between the two particles. The angular momentum $\hat{\boldsymbol{L}}_1 = \hat{\boldsymbol{r}}_1 \times \hat{\boldsymbol{p}}_1$ commutes with $\hat{H}_{01}$.

$$[\hat{H}_{01}, \hat{\boldsymbol{L}}_1] = 0 .$$

We note that all observables relating to one of the particles (particle 1, in our case) commute with all those corresponding to the other one (particle 2, in our case).

$$[\hat{H}_{02}, \hat{\boldsymbol{L}}_1] = 0 .$$

which means that

$$[\hat{H}_{01} + \hat{H}_{02}, \hat{L}_1] = 0 \,,$$

Similarly, we get

$$[\hat{H}_{01}, \hat{L}_2] = 0 \,, \qquad\qquad [\hat{H}_{02}, \hat{L}_2] = 0$$

which means that

$$[\hat{H}_{01} + \hat{H}_{02}, \hat{L}_2] = 0$$

Then we have

$$[\hat{H}_{01} + \hat{H}_{02}, \hat{L}] = 0$$

where

$$\hat{L} = \hat{L}_1 + \hat{L}_2 \,.$$

How about the commutation relation on $[\hat{H}, \hat{L}] = 0$? We note that

$$[\hat{H}, \hat{L}] = [\hat{H}_{01} + \hat{H}_{02} + \hat{H}_1, \hat{L}] = [\hat{H}_1, \hat{L}]$$

Using the Mathematica, we show that

$$[\hat{H}_1, \hat{L}] = 0 \,.$$

or

$$\langle r_1, r_2 | [\hat{H}_1, \hat{L}_z] | \psi \rangle = H_1(|r_1 - r_2|) L_z \psi(r_1, r_2) - L_z H_1(|r_1 - r_2|) \psi(r_1, r_2)$$

where

$$H_1(|r_1 - r_2|) = \frac{e^2}{|r_1 - r_2|}, \qquad\qquad L_z = L_{1z} + L_{2z},$$

$$L_{1z} = \frac{\hbar}{i}\left(x_1 \frac{\partial}{\partial y_1} - y_1 \frac{\partial}{\partial x_1}\right), \qquad L_{2z} = \frac{\hbar}{i}\left(x_2 \frac{\partial}{\partial y_2} - y_2 \frac{\partial}{\partial x_2}\right),$$

$$r_1 = (x_1, y_1, z_1), \qquad\qquad r_2 = (x_2, y_2, z_2).$$

((Mathematica))

```
Clear["Global`*"];

R12 = √((x1 - x2)² + (y1 - y2)² + (z1 - z2)²) ; H3 = e1²/R12 ;

L1z := ℏ/i (x1 D[#, y1] - y1 D[#, x1]) &;

L2z := ℏ/i (x2 D[#, y2] - y2 D[#, x2]) &;

Lz := (L1z[#] + L2z[#]) &;

ψ1 = ψ[x1, y1, z1, x2, y2, z2];

H3 Lz[ψ1] - Lz[H3 ψ1] // Simplify

0
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Then we have the commutation relation

$$[\hat{H}, \hat{L}] = 0,$$

or

$$[\hat{H}, \hat{L}_x] = 0, \quad [\hat{H}, \hat{L}_y] = 0, \quad [\hat{H}, \hat{L}_z] = 0$$

From these relations, we have

$$[\hat{H}, \hat{L}^2] = 0, \quad \text{and} \quad [\hat{H}, \hat{L}_z] = 0$$

Similarly we have

$$[\hat{H}, \hat{S}^2] = 0, \quad [\hat{H}, \hat{S}_z] = 0$$

Here

$$[\hat{L}_i, \hat{S}_j] = 0$$

The total angular momentum is defined by

$$J = L + S.$$

We note that

$$[\hat{H}, \hat{L}] = 0, \quad [\hat{H}, \hat{S}] = 0, \quad [\hat{H}, \hat{L}^2] = 0, \quad [\hat{H}, \hat{S}^2] = 0,$$

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From this relation we find that

$$[\hat{H},\hat{J}]=[\hat{H},\hat{L}]+[\hat{H},\hat{S}]=0.$$

leading to

$$[\hat{H},\hat{J}^2]=0, \quad [\hat{H},\hat{J}_z]=0$$

In summary, there is a simultaneous eigenket of the operators $\hat{L}^2$, $\hat{S}^2$, $\hat{L}_z$, and $\hat{S}_z$. So the total angular momentum and the total spin angular momentum are good quantum numbers which denote the resulting states.

4. Spin state for the total Hamiltonian $\hat{H}$

From the above discussion, we have

$$[\hat{H},\hat{S}_z]=0, \quad [\hat{H},\hat{S}^2]=0, \quad [\hat{P}_{12}{}^{spin},\hat{H}]=0.$$

$$[\hat{S}^2,\hat{S}_z]=0$$

So we have the simultaneous eigenket of $\hat{P}_{12}{}^{spin}$, $\hat{S}^2$, and $\hat{S}_z$.

(i) $S=1$

$$\left|\chi_s{}^{spin}\right\rangle = \begin{cases} \left|S=1,M_s=1\right\rangle = \left|++\right\rangle \\ \left|S=1,M_s=0\right\rangle = \dfrac{1}{\sqrt{2}}(\left|+-\right\rangle+\left|-+\right\rangle) \\ \left|S=1,M_s=-1\right\rangle = \left|--\right\rangle \end{cases}. \qquad \text{(symmetric)}$$

with

$$\hat{P}_{12}{}^{spin}\left|\chi_s{}^{spin}\right\rangle = \left|\chi_s{}^{spin}\right\rangle, \qquad \hat{P}_{12}{}^{spin}\left|S,M_s\right\rangle = (-1)^{S+1}\left|S,M_s\right\rangle$$

(ii) $S=0$

$$\left|\chi_a{}^{spin}\right\rangle = \left|S=0,M_s=0\right\rangle \dfrac{1}{\sqrt{2}}(\left|+-\right\rangle-\left|-+\right\rangle). \quad \text{(anti-symmetyric)}$$

with

$$\hat{P}_{12}{}^{spin}\left|\chi_a{}^{spin}\right\rangle = -\left|\chi_a{}^{spin}\right\rangle \qquad \hat{P}_{12}{}^{spin}\left|S,M_s\right\rangle = (-1)^{S+1}\left|S,M_s\right\rangle$$

5. Orbital state for the total Hamiltonian $\hat{H}$

We need to choose the unperturbed states that diagonalize the perturbation **(Cardinal rule).** So the best way we can do is to choose the state

$$|L,M;n_1,l_1;n_2,l_2\rangle = \text{the superposition of the kets } |n_1,l_1,m_1\rangle \text{ and } |n_2,l_2,m_2\rangle \text{ with the}$$
$$\text{Clebsch-Gordan co-efficients}$$

with

$$M = m_1 + m_2, \qquad L = l_1 + l_2, l_1 + l_2 - 1,..., |l_1 - l_2|,$$

where L and M are the good quantum numbers. Here we use the following notation.

$$L^2 = \hbar^2 L(L+1), \qquad L_z = \hbar M,$$

with

$$M = m_1 + m_2,$$

where

$$m_1 = l_1, l_1\text{-}1, l_1 \text{-}2, \ldots, \text{-} l_1,$$

$$m_2 = l_2, l_2\text{-} 1, l_2\text{-}2, \ldots, \text{-} l_2.$$

7. Eigenstates $|L,M;n_1,l_1;n_2,l_2\rangle$ (Cohen-Tannoudji))

$$\hat{P}_{12} = \hat{P}_{12}^{(space)} \hat{P}_{12}^{(spin)},$$

$$|\psi\rangle = c(\hat{1} - \hat{P}_{12})|L,M;n_1,l_1;n_2,l_2\rangle \otimes |S,M_S\rangle$$
$$= c(\hat{1} - \hat{P}_{12}^{(space)} \hat{P}_{12}^{(spin)})|L,M;n_1,l_1;n_2,l_2\rangle \otimes |S,M_S\rangle,$$

where c is a normalization constant, and $|L,M;n_1,l_1;n_2,l_2\rangle$ are formed of the superposition of the kets $|n_1,l_1,m_1\rangle$ and $|n_2,l_2,m_2\rangle$ with the Clebsch-Gordan co-efficients.

$$\hat{P}_{12}^{(spin)}|S,M_S\rangle = (-1)^{S+1}|S,M_S\rangle.$$

where

$$\hat{P}_{12}^{(spin)}|S=1,M_S\rangle = (-1)^2|S=1,M_S\rangle = |S=1,M_S\rangle \quad \text{(symmetric)}$$

$$\hat{P}_{12}{}^{(spin)}\big|S=0,M_S=0\big\rangle=(-1)^1\big|S=0,0\big\rangle=-\big|S=0,0\big\rangle \quad \text{(antisymmetric)}$$

The symmetrizer operator and antisymmetrizer operator are defined by

$$\hat{A}^{(space)}=\frac{1}{\sqrt{2}}[1-\hat{P}_{12}{}^{(space)}],\qquad \hat{S}^{(space)}=\frac{1}{\sqrt{2}}[1+\hat{P}_{12}{}^{(space)}]$$

(i) $\big|n_1,l_1\big\rangle\neq\big|n_2,l_2\big\rangle$

$$\big|\psi\big\rangle=c[\hat{1}-(-1)^{S+1}\hat{P}_{12}{}^{(space)})\big|L,M;n_1,l_1;n_2,l_2\big\rangle\otimes\big|S,M_S\big\rangle.$$

When $S=1$ (symmetric)

$$\begin{aligned}\big|\psi\big\rangle&=c(\hat{1}-\hat{P}_{12}{}^{(space)})\big|L,M;n_1,l_1;n_2,l_2\big\rangle\otimes\big|S,M_S\big\rangle\\&=c\sqrt{2}\hat{A}^{(space)}\big|L,M;n_1,l_1;n_2,l_2\big\rangle\otimes\big|S,M_S\big\rangle\end{aligned}.$$

When $S=0$ (antisymmetric),

$$\begin{aligned}\big|\psi\big\rangle&=c(\hat{1}+\hat{P}_{12}{}^{(space)})\big|L,M;n_1,l_1;n_2,l_2\big\rangle\otimes\big|S,M_S\big\rangle\\&=c\sqrt{2}\hat{S}^{(space)}\big|L,M;n_1,l_1;n_2,l_2\big\rangle\otimes\big|S,M_S\big\rangle\end{aligned}$$

(ii) $\big|n_1,l_1\big\rangle=\big|n_2,l_2\big\rangle$

$$\big|\psi\big\rangle=c[\hat{1}-(-1)^{S+1}\hat{P}_{12}{}^{(space)})\big|L,M;n_1,l_1;n_2,l_2\big\rangle\otimes\big|S,M_S\big\rangle.$$

We use the formula,

$$\hat{P}_{12}{}^{(space)}\big|L,M;n_1,l_1;n_2,l_2\big\rangle=(-1)^L\big|L,M;n_1,l_1;n_2,l_2\big\rangle,$$

only for $\big|n_1,l_1\big\rangle=\big|n_2,l_2\big\rangle$ (the same state such as $\big|1s\big\rangle_1\big|1s\big\rangle_2$, $\big|2p\big\rangle_1\big|2p\big\rangle_2$). This will be shown later from the discussion of the Clebsch-Gordan coefficients. Then we have

$$\big|\psi\big\rangle=c[\hat{1}-(-1)^{L+S+1})\big|L,M;n_1,l_1;n_2,l_2\big\rangle\otimes\big|S,M_S\big\rangle.$$

When $L+S=$ even,

$$\big|\psi\big\rangle=2c\big|L,M;n_1,l_1;n_2,l_2\big\rangle\otimes\big|S,M_S\big\rangle.$$

((**Example**)) Two electron systems with spin 1/2

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$S = 1$ (symm) and $L = 1$ (antisymm)
$S = 0$ (antisymm) and $L = 0$ (symm).

When $L + S =$ odd,

$$\left|\psi\right\rangle = 0.$$

Here we show the Clebsh-Gordan coefficients for the two particles in the same or the different orbital states.

Clebsh-Gordan coefficients

(1s)(1s), (1s)(2s), (1s)(3s), (2s)(2s)

$L = 0$ (symmetric)

$$\left|L = 0, M_L = 0\right\rangle = \left|l_1 = 0, m_1 = 0\right\rangle\left|l_2 = 0, m_2 = 0\right\rangle$$
$$= \left|0,0\right\rangle_1\left|0,0\right\rangle_2$$

(1s)(2p), (1s)(3p), (2s)(2p)

$L = 1$

$$\left|L = 1, M_L = 1\right\rangle = \left|1,1\right\rangle_1\left|0,0\right\rangle_2,$$

$$\left|L = 1, M_L = 0\right\rangle = \left|1,0\right\rangle_1\left|0,0\right\rangle_2,$$

$$\left|L = 1, M_L = -1\right\rangle = \left|1,-1\right\rangle_1\left|0,0\right\rangle_2.$$

(2p)(2p), (2p)(3p)

$L = 2$ (symmetric)

$$\left|L = 2, M_L = 2\right\rangle = \left|1,1\right\rangle_1\left|1,1\right\rangle_2,$$

$$\left|L = 2, M_L = 1\right\rangle = \frac{1}{\sqrt{2}}(\left|1,1\right\rangle_1\left|1,0\right\rangle_2 + \left|1,0\right\rangle_1\left|1,1\right\rangle_2),$$

$$\left|L = 2, M_L = 0\right\rangle = \frac{1}{\sqrt{6}}(\left|1,1\right\rangle_1\left|1,-1\right\rangle_2 + \left|1,-1\right\rangle_1\left|1,1\right\rangle_2 + 2\left|1,0\right\rangle_1\left|1,0\right\rangle_2),$$

$$\left|L = 2, M_L = -1\right\rangle = \frac{1}{\sqrt{2}}(\left|1,-1\right\rangle_1\left|1,0\right\rangle_2 + \left|1,0\right\rangle_1\left|1,-1\right\rangle_2),$$

$$\left|L = 2, M_L = -2\right\rangle = \left|1,-1\right\rangle_1\left|1,-1\right\rangle_2.$$

$$\left|L=1,M_L=1\right\rangle = \frac{1}{\sqrt{2}}\left(\left|1,1\right\rangle_1\left|1,0\right\rangle_2 - \left|1,0\right\rangle_1\left|1,1\right\rangle_2\right),$$

$$\left|L=1,M_L=0\right\rangle = \frac{1}{\sqrt{2}}\left(\left|1,1\right\rangle_1\left|1,-1\right\rangle_2 - \left|1,-1\right\rangle_1\left|1,1\right\rangle_2\right),$$

$$\left|L=1,M_L=-1\right\rangle = \frac{1}{\sqrt{2}}\left(\left|1,0\right\rangle_1\left|1,-1\right\rangle_2 - \left|1,-1\right\rangle_1\left|1,0\right\rangle_2\right).$$

$L = 0$ (symmetric)

$$\left|L=0,M_L=0\right\rangle = \frac{1}{\sqrt{3}}\left(\left|1,1\right\rangle_1\left|1,-1\right\rangle_2 + \left|1,-1\right\rangle_1\left|1,1\right\rangle_2 - \left|1,0\right\rangle_1\left|1,0\right\rangle_2\right).$$

(2p)(3d), (3p)(3d)

$L = 3$

$$\left|L=3,M_L=3\right\rangle = \left|1,1\right\rangle_1\left|2,2\right\rangle_2,$$

$$\left|L=3,M_L=2\right\rangle = \sqrt{\frac{2}{3}}\left|1,1\right\rangle_1\left|2,1\right\rangle_2 + \frac{1}{\sqrt{3}}\left|1,0\right\rangle_1\left|2,2\right\rangle_2,$$

$$\left|L=3,M_L=1\right\rangle = \sqrt{\frac{2}{5}}\left|1,1\right\rangle_1\left|2,0\right\rangle_2 + 2\sqrt{\frac{2}{15}}\left|1,0\right\rangle_1\left|2,1\right\rangle_2 + \frac{1}{\sqrt{15}}\left|1,-1\right\rangle_1\left|2,2\right\rangle_2,$$

$$\left|L=3,M_L=0\right\rangle = \frac{1}{\sqrt{5}}\left|1,1\right\rangle_1\left|2,-1\right\rangle_2 + \sqrt{\frac{3}{5}}\left|1,0\right\rangle_1\left|2,0\right\rangle_2 + \frac{1}{\sqrt{5}}\left|1,-1\right\rangle_1\left|2,1\right\rangle_2,$$

$$\left|L=3,M_L=-1\right\rangle = \sqrt{\frac{2}{5}}\left|1,-1\right\rangle_1\left|2,0\right\rangle_2 + 2\sqrt{\frac{2}{15}}\left|1,0\right\rangle_1\left|2,-1\right\rangle_2 + \frac{1}{\sqrt{15}}\left|1,1\right\rangle_1\left|2,-2\right\rangle_2,$$

$$\left|L=3,M_L=2\right\rangle = \sqrt{\frac{2}{3}}\left|1,-1\right\rangle_1\left|2,-1\right\rangle_2 + \frac{1}{\sqrt{3}}\left|1,0\right\rangle_1\left|2,-2\right\rangle_2,$$

$$\left|L=3,M_L=3\right\rangle = \left|1,-1\right\rangle_1\left|2,-2\right\rangle_2.$$

$L = 2$

$$\left|L=2,M_L=2\right\rangle = -\sqrt{\frac{2}{3}}\left|1,0\right\rangle_1\left|2,2\right\rangle_2 + \frac{1}{\sqrt{3}}\left|1,1\right\rangle_1\left|2,1\right\rangle_2$$

$$\left|L=2,M_L=1\right\rangle = \frac{1}{\sqrt{2}}\left|1,1\right\rangle_1\left|2,0\right\rangle_2 - \frac{1}{\sqrt{6}}\left|1,0\right\rangle_1\left|2,1\right\rangle_2 - \frac{1}{\sqrt{3}}\left|1,-1\right\rangle_1\left|2,2\right\rangle_2,$$

$$\left|L=2,M_L=0\right\rangle = \frac{1}{\sqrt{2}}\left|1,1\right\rangle_1\left|2,-1\right\rangle_2 - \frac{1}{\sqrt{2}}\left|1,-1\right\rangle_1\left|2,1\right\rangle_2,$$

$$|L=2, M_L = -1\rangle = \frac{1}{\sqrt{3}}|1,1\rangle_1|2,-2\rangle_2 + \frac{1}{\sqrt{6}}|1,0\rangle_1|2,-1\rangle_2 - \frac{1}{\sqrt{2}}|1,-1\rangle_1|2,0\rangle_2,$$

$$|L=2, M_L = -2\rangle = \sqrt{\frac{2}{3}}|1,0\rangle_1|2,-2\rangle_2 - \frac{1}{\sqrt{3}}|1,1\rangle_1|2,1\rangle_2.$$

$L = 1$

$$|L=1, M_L = 1\rangle = \frac{1}{\sqrt{10}}|1,1\rangle_1|2,0\rangle_2 - \sqrt{\frac{3}{10}}|1,0\rangle_1|2,1\rangle_2 - \sqrt{\frac{3}{5}}|1,-1\rangle_1|2,2\rangle_2,$$

$$|L=1, M_L = 0\rangle = \sqrt{\frac{3}{10}}|1,1\rangle_1|2,-1\rangle_2 - \sqrt{\frac{2}{5}}|1,0\rangle_1|2,0\rangle_2 + \sqrt{\frac{3}{10}}|1,-1\rangle_1|2,1\rangle_2,$$

$$|L=1, M_L = -1\rangle = \frac{1}{\sqrt{10}}|1,-1\rangle_1|2,0\rangle_2 - \sqrt{\frac{3}{10}}|1,0\rangle_1|2,-1\rangle_2 + \sqrt{\frac{3}{5}}|1,1\rangle_1|2,-2\rangle_2.$$

6. Ground state

Here we discuss the eigenvalue and eigenfunction of the system. The unperturbed $\hat{H}_0$ is just the sum of two independent Coulomb Hamiltonians. Thus we can express the eigenstate of $\hat{H}_0$ as simultaneous hydrogen eigenstates:

$$|n_1, l_1, m_1\rangle \otimes |n_2, l_2, m_2\rangle.$$

On the other hand, the full Hamiltonian $\hat{H}$ is too complicated to solve directly. So we must resort to approximation methods.

Let us start with the ground state of $\hat{H}_0$. Since

$$\begin{aligned}|\psi_{space}\rangle &= |n=1, l=0, m=0\rangle \otimes |n=1, l=0, m=0\rangle \\ &= |1s\rangle \otimes |1s\rangle\end{aligned},$$

is symmetrical (space part), the spin part should be anti-symmetric,

$$|\chi_{spin}\rangle = \frac{1}{\sqrt{2}}[(|+,-\rangle - |-,+\rangle] \qquad (S = 0, \text{ singlet}).$$

Then the ground state of the two electrons is given by $|\psi_{space}\rangle|\chi_{spin}\rangle$.

$$E(1s,1s)^{(0)} = 2(-\frac{1}{2}m_e c^2 Z^2 \alpha^2) = -8(13.6eV) = -108.8eV,$$

where $Z = 2$. The ground state wave function is given by

$$\langle r|100\rangle = R_{10}(r)Y_0^0(\theta,\phi) = \frac{1}{\sqrt{\pi}}(\frac{Z}{a_0})^{3/2}e^{-\frac{Zr}{a_0}} .$$

The first-order shift in the ground state

$$E(1s,1s)^{(1)} = \langle 1s,1s|\hat{H}_1|1s,1s\rangle = \frac{5}{8}Zm_ec^2\alpha^2 = 34.0eV ,$$

with

$$\langle 1s,1s|\hat{H}_1|1s,1s\rangle = \iint d^3r_1d^3r_2|\langle r_1|100\rangle|^2|\langle r_2|100\rangle|^2\frac{e^2}{r_{12}} .$$

Then we get

$$E(1s,1s) = E(1s,1s)^{(0)} + E(1s,1s)^{(1)} = -108.8 + 34.0 = -74.8eV ,$$

in comparison with the experimental result: -78.975 eV.

Here we note

$$E_n^{(0)} = -\frac{1}{2}m_ec^2\frac{(Z\alpha)^2}{n^2} = -\frac{R}{n^2}Z^2 ,$$

with

$$R = 13.60569253(30) \text{ eV}$$

Fine structure constant;

$$\alpha = \frac{e^2}{\hbar c} .$$

Bohr radius:

$$a_B = a_0 = \frac{\hbar^2}{m_e e^2} .$$

$$\frac{e^2}{a_0} = m_ec^2\alpha^2 = 2\times\frac{1}{2}m_ec^2\alpha^2 .$$

((Note))

$$\frac{1}{r_{12}} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta}},$$

$$\int_0^\pi \sin\theta d\theta \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\theta}} = \frac{4}{r_1 + r_2 + |r_1 - r_2|},$$

$$\iint d^3r_1 d^3r_2 \left|\langle \mathbf{r}_1 | 100 \rangle\right|^2 \left|\langle \mathbf{r}_2 | 100 \rangle\right|^2 \frac{e^2}{r_{12}} = \int d^3r_1 \left|\langle \mathbf{r}_1 | 100 \rangle\right|^2 \int d^3r_2 \left|\langle \mathbf{r}_2 | 100 \rangle\right|^2 \frac{e^2}{r_{12}},$$
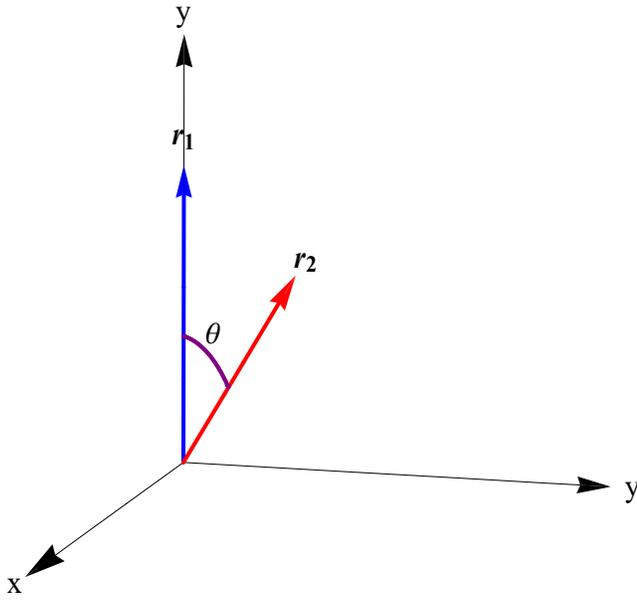
Fig. First we fix the direction of $\mathbf{r}_1$ in the z axis. θ is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$.
$\mathbf{r}_1 = (r_1 \sin\theta \cos\phi, r_1 \sin\theta \sin\phi, r_1 \cos\theta)$

$$\int d^3 r_2 \left|\langle r_2|100\rangle\right|^2 \frac{1}{r_{12}} = \int r_2{}^2 dr_2 \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 e^{-\frac{2Zr_2}{a_0}} \frac{1}{\sqrt{r_1{}^2 + r_2{}^2 - 2r_1 r_2 \cos\theta}}$$

$$= 2\pi \int \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 r_2{}^2 e^{-\frac{2Zr_2}{a_0}} dr_2 \int_0^{\pi} \sin\theta d\theta \frac{1}{\sqrt{r_1{}^2 + r_2{}^2 - 2r_1 r_2 \cos\theta}}$$

$$= 2\left(\frac{Z}{a_0}\right)^3 \int r_2{}^2 e^{-\frac{2Zr_2}{a_0}} dr_2 \frac{4}{r_1 + r_2 + |r_1 - r_2|}$$

$$= 8\left(\frac{Z}{a_0}\right)^3 \int r_2{}^2 e^{-\frac{2Zr_2}{a_0}} dr_2 \frac{1}{r_1 + r_2 + |r_1 - r_2|}$$

$$= 8\left(\frac{Z}{a_0}\right)^3 \int_0^{\infty} r_2{}^2 dr_2 e^{-\frac{2Zr_2}{a_0}} \frac{1}{r_1 + r_2 + |r_1 - r_2|}$$

Then we have

$$\int d^3 r_2 \left|\langle r_2|100\rangle\right|^2 \frac{1}{r_{12}} = 8\left(\frac{Z}{a_0}\right)^3 \left[\int_0^{r_1} r_2{}^2 dr_2 e^{-\frac{2Zr_2}{a_0}} \frac{1}{2r_1} + \int_{r_1}^{\infty} r_2{}^2 dr_2 e^{-\frac{2Zr_2}{a_0}} \frac{1}{2r_2}\right]$$

$$= 4\left(\frac{Z}{a_0}\right)^3 \left[\int_0^{r_1} \frac{r_2{}^2}{r_1} dr_2 e^{-\frac{2Zr_2}{a_0}} + \int_{r_1}^{\infty} r_2 dr_2 e^{-\frac{2Zr_2}{a_0}}\right]$$

$$= 4\left(\frac{Z}{a_0}\right)^3 g(r_1)$$

$$\iint d^3 r_1 d^3 r_2 \left|\langle r_1|100\rangle\right|^2 \left|\langle r_2|100\rangle\right|^2 \frac{1}{r_{12}} = 4\left(\frac{Z}{a_0}\right)^3 \int d^3 r_1 \left|\langle r_1|100\rangle\right|^2 g(r_1)$$

$$= 4\left(\frac{Z}{a_0}\right)^3 \int 2\pi r_1{}^2 g(r_1) dr_1 \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3 e^{-\frac{2Zr_1}{a_0}} 1$$

$$= 8\left(\frac{Z}{a_0}\right)^6 \int_0^{\infty} dr_1 r_1{}^2 g(r_1) e^{-\frac{2Zr_1}{a_0}}$$

Finally we get

$$\iint d^3 r_1 d^3 r_2 \left|\langle r_1|100\rangle\right|^2 \left|\langle r_2|100\rangle\right|^2 \frac{e^2}{r_{12}} = 8e^2 \left(\frac{Z}{a_0}\right)^6 \frac{5a_0{}^5}{128Z^5} = \frac{5e^2 Z}{16 a_0},$$

$$\boxed{\langle 1s,1s|\hat{H}_1|1s,1s\rangle = \frac{5Z}{8}\frac{1}{2}m_e c^2 \alpha^2 .}$$

((Mathematica))

```
Clear["Global`*"]; ψ[n_, ℓ_, m_, r_, θ_, φ_] :=
  1/(√((n + ℓ)!))
  (2^(1+ℓ) a^(-ℓ-3/2) e^(-Z1 r/(a n)) n^(-ℓ-2) Z1^(ℓ+3/2) r^ℓ √((n - ℓ - 1)!)

     LaguerreL[-1 + n - ℓ, 1 + 2 ℓ, (2 Z1 r)/(a n)])

   SphericalHarmonicY[ℓ, m, θ, φ];
ψ1s[r_] := ψ[1, 0, 0, r, θ, φ];

ψ2s[r_] := ψ[2, 0, 0, r, θ, φ];

        e1²
f1 = ─────────────────────────── ;
    √(r1² + r2² - 2 r1 r2 Cos[θ])

eq1 = Integrate[2 π Sin[θ] f1, {θ, 0, π}] //
   Simplify[#, {r1 > 0, r2 > 0, (r1 - r2)² > 0}] &;
f11 = eq1 // Simplify[#, r2 < r1] &; f12 = eq1 // Simplify[#, r2 > r1] &;
g11 = r2² ψ1s[r2]² f11 ; g12 = r2² ψ1s[r2]² f12 ;
a1 = Integrate[g11, {r2, 0, r1}] // FullSimplify;

a2 = Integrate[g12, {r2, r1, ∞}] // FullSimplify[#, Re[Z1/a] > 0] &;

a12 = (a1 + a2) // Simplify; a3 = a12 4 π r1² ψ1s[r1]² ;

Integrate[a3, {r1, 0, ∞}] // FullSimplify[#, Re[Z1/a] > 0] &

5 e1² Z1
────────
  8 a
```

7.   Variational method

Suppose that the wave function of the ground state is given by

$$\left\langle r | 100(\bar{Z}) \right\rangle = \frac{1}{\sqrt{\pi}} \left(\frac{\bar{Z}}{a_0}\right)^{3/2} e^{-\frac{\bar{Z} r}{a_0}} \, .$$

The Hamiltonian is given by

$$\hat{H} = \frac{1}{2m_e}\hat{\mathbf{p}}_1{}^2 + \frac{1}{2m_e}\hat{\mathbf{p}}_2{}^2 - \frac{Ze^2}{|\hat{\mathbf{r}}_1|} - \frac{Ze^2}{|\hat{\mathbf{r}}_2|} + \frac{e^2}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|}$$

$$= [\frac{1}{2m_e}\hat{\mathbf{p}}_1{}^2 - \frac{\bar{Z}e^2}{|\hat{\mathbf{r}}_1|} + \frac{1}{2m_e}\hat{\mathbf{p}}_2{}^2 - \frac{\bar{Z}e^2}{|\hat{\mathbf{r}}_2|}]$$

$$+ [\frac{(\bar{Z}-Z)e^2}{|\hat{\mathbf{r}}_1|} + \frac{(\bar{Z}-Z)e^2}{|\hat{\mathbf{r}}_2|}] + \frac{e^2}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|}$$

Here we calculate the expectation value $\langle E \rangle = \langle \psi | \hat{H} | \psi \rangle$

$$\langle E \rangle_1 = -\frac{1}{2}m_e c^2 (\bar{Z}\alpha)^2 (1+1) = \frac{1}{2}m_e c^2 \alpha^2 (-2\bar{Z}^2),$$

$$\langle E \rangle_2 = \int d^3 r_1 \int d^3 r_2 \left| \langle r_1 | 100(\bar{Z}) \rangle \right|^2 \frac{(\bar{Z}-Z)e^2}{r_1} \left| \langle r_2 | 100(\bar{Z}) \rangle \right|^2$$

$$= \frac{e^2}{a_0} \bar{Z}(\bar{Z}-Z)$$

$$= m_e c^2 \alpha^2 \bar{Z}(\bar{Z}-Z)$$

$$\langle E \rangle_3 = \int d^3 r_1 \int d^3 r_2 \left| \langle r_1 | 100(\bar{Z}) \rangle \right|^2 \frac{(\bar{Z}-Z)e^2}{r_2} \left| \langle r_2 | 100(\bar{Z}) \rangle \right|^2$$

$$= \frac{e^2}{a_0} \bar{Z}(\bar{Z}-Z)$$

$$= m_e c^2 \alpha^2 \bar{Z}(\bar{Z}-Z)$$

$$\langle E \rangle_4 = \int d^3 r_1 \int d^3 r_2 \left| \langle r_1 | 100(\bar{Z}) \rangle \right|^2 \frac{e^2}{|r_1 - r_2|} \left| \langle r_2 | 100(\bar{Z}) \rangle \right|^2$$

$$= \frac{5}{8} \bar{Z} m_e c^2 \alpha^2$$

Then

$$\langle E \rangle = \langle \psi | \hat{H} | \psi \rangle = \frac{1}{2} m_e c^2 \alpha^2 [-2\bar{Z}^2 + 4\bar{Z}(\bar{Z}-Z) + \frac{5}{4}\bar{Z}],$$

We find the minimum energy from the derivative of $\langle E \rangle$ with respect to $\bar{Z}$,

$$E_0 = -\frac{1}{2}m_e c^2 \alpha^2 \frac{1}{128}(5-16Z)^2 = -\frac{1}{2}m_e c^2 \alpha^2 2(Z - \frac{5}{16})^2 \ .$$

When $Z = 2$,

$$E = -\frac{1}{2} m_e c^2 \alpha^2 2(Z - \frac{5}{16})^2 = -2 \times 13.60569253 \text{ eV} \times (2 - \frac{5}{16})^2 = \text{-77.4563 eV}$$

where

$$\overline{Z} = Z - \frac{5}{16} = 1.6875 .$$

This result of E is comparable with the experimental result: -78.975 eV.

((Mathematica))

```
Clear["Global`*"]; ϕ[r_] := (Z1/a0)^(3/2) 1/√π Exp[-Z1/a0 r];

g1 =
 Integrate[ϕ[r1]^2 4 π r1^2/r1 4 π r2^2 e1^2 (Z1 - Z) ϕ[r2]^2,

  {r1, 0, ∞}] // Simplify[#, Re[Z1/a0] > 0] &;

 Integrate[g1 , {r2, 0, ∞}] //
  Simplify[#, Re[Z1/a0] > 0] &

 e1^2 Z1 (-Z + Z1)
 ─────────────────
        a0
```

Minimum energy determination: Z1 = x. x is changed as a variable. z is fixed as z = 2 for He.

```
h1 = -2 x² + 4 x (x - z) + 5/4 x // Simplify
```

$$\frac{1}{4} x (5 + 8 x - 16 z)$$

```
h2 = Solve[D[h1, x] == 0, x]
```

$$\left\{\left\{x \to \frac{1}{16} (-5 + 16 z)\right\}\right\}$$

```
h11 = h1 /. h2[[1]] // FullSimplify
```

$$-\frac{1}{128} (5 - 16 z)^2$$

```
-27.2 (z - 5/16)² /. z → 2
```

$$-77.4563$$

---

8. First excited state

We consider the (1s)(2s) electron configuration, where one electron is in the 1s state and the other is in the 2s state. We note that the addition of the orbital angular momentum leads to

$L = 0$.   (the total orbital angular momentum)

Here we do not use the Clebsch-Gordan c-efficient to find the wave functions.

(1)

$$\left|1s+\right\rangle_1\left|2s+\right\rangle_2 - \left|2s+\right\rangle_1\left|1s+\right\rangle_2 = \left[\left|1s\right\rangle_1\left|2s\right\rangle_2 - \left|2s\right\rangle_1\left|1s\right\rangle_2\right]\left|+,+\right\rangle.$$

(2)

$$\left|1s+\right\rangle_1\left|2s-\right\rangle_2 - \left|2s-\right\rangle_1\left|1s+\right\rangle_2 = \left|1s\right\rangle_1\left|2s\right\rangle_2\left|+,-\right\rangle - \left|2s\right\rangle_1\left|1s\right\rangle_2\left|-,+\right\rangle.$$

(3)

$$\left|1s-\right\rangle_1\left|2s+\right\rangle_2 - \left|2s+\right\rangle_1\left|1s-\right\rangle_2 = \left|1s\right\rangle_1\left|2s\right\rangle_2\left|-,+\right\rangle - \left|2s\right\rangle_1\left|1s\right\rangle_2\left|+,-\right\rangle.$$

(4)

$$\left|1s-\right\rangle_1\left|2s-\right\rangle_2 - \left|2s-\right\rangle_1\left|1s-\right\rangle_2 = \left[\left|1s\right\rangle_1\left|2s\right\rangle_2 - \left|2s\right\rangle_1\left|1s\right\rangle_2\right]\left|-,-\right\rangle.$$

Eq.(2) + Eq.(3):

$$[|1s\rangle_1|2s\rangle_2|+,-\rangle - |2s\rangle_1|1s\rangle_2|-,+\rangle] + [|1s\rangle_1|2s\rangle_2|-,+\rangle - |2s\rangle_1|1s\rangle_2|+,-\rangle],$$

which is equal to

$$[|1s\rangle_1|2s\rangle_2 - |2s\rangle_1|1s\rangle_2]\frac{|+,-\rangle + |-,+\rangle}{\sqrt{2}}.$$

Eq.(2) - Eq.(3):

$$[|1s\rangle_1|2s\rangle_2|+,-\rangle - |2s\rangle_1|1s\rangle_2|-,+\rangle] - [|1s\rangle_1|2s\rangle_2|-,+\rangle - |2s\rangle_1|1s\rangle_2|+,-\rangle],$$

which is equal to

$$[|1s\rangle_1|2s\rangle_2 + |2s\rangle_1|1s\rangle_2]\frac{|+,-\rangle - |-,+\rangle}{\sqrt{2}}.$$

The zero-th order wave function for the first excited state

(i) The antisymmetric orbital state;

$$\frac{|1s\rangle_1|2s\rangle_2 - |2s\rangle_1|1s\rangle_2}{\sqrt{2}} = |\psi_A\rangle,$$

where the spin state is symmetric ($S = 1$, triplet state)

(ii) The symmetric orbital state;

$$\frac{|1s\rangle_1|2s\rangle_2 + |2s\rangle_1|1s\rangle_2}{\sqrt{2}} = |\psi_s\rangle,$$

where the spin state is anti-symmetric ($S = 0$, singlet state).
    Here we use the notation $|\psi_+\rangle = |\psi_s\rangle$ for the symmetric state and the notation $|\psi_-\rangle = |\psi_a\rangle$ for the antisymmetric state.

$$\langle r',r''|\psi_\pm\rangle = \psi_\pm(r',r'') = \frac{1}{\sqrt{2}}[\langle r'|1s\rangle\langle r''|2s\rangle \pm \langle r'|2s\rangle\langle r''|1s\rangle].$$

Now we calculate the matrix element

$$\langle \psi_\pm | \hat{H}_1 | \psi_\pm \rangle = \iint d^3 r' d^3 r'' \psi_\pm^{\,*}(r',r'') H_1(r',r'') \psi_\pm(r',r'')$$

$$= \frac{1}{2} \iint d^3 r' d^3 r'' [\langle r'|1s\rangle^* \langle r''|2s\rangle^* \pm \langle r'|2s\rangle^* \langle r''|1s\rangle^*] H_1(r',r'')$$

$$[\langle r'|1s\rangle \langle r''|2s\rangle \pm \langle r'|2s\rangle \langle r''|1s\rangle]$$

Calculation of the matrix elements: (perturbation for the degenerate system)
We assume that

$$H_1(r',r'') = \frac{e^2}{|r'-r''|}.$$

Then we have

$$\langle \psi_+ | \hat{H}_1 | \psi_+ \rangle = \iint d^3 r' d^3 r'' \psi_+^{\,*}(r',r'') H_1(r',r'') \psi_+(r',r'')$$

$$= \frac{1}{2} \iint d^3 r' d^3 r'' [\langle r'|1s\rangle^* \langle r''|2s\rangle^* + \langle r'|2s\rangle^* \langle r''|1s\rangle^*] H_1(r',r'')$$

$$[\langle r'|1s\rangle \langle r''|2s\rangle + \langle r'|2s\rangle \langle r''|1s\rangle]$$

$$= \frac{V_{11} + V_{12} + V_{21} + V_{22}}{2}$$

$$= J + \frac{K + K^*}{2}$$

$$\langle \psi_+ | \hat{H}_1 | \psi_- \rangle = \iint d^3 r' d^3 r'' \psi_+^{\,*}(r',r'') H_1(r',r'') \psi_-(r',r'')$$

$$= \frac{1}{2} \iint [\langle r'|1s\rangle^* \langle r''|2s\rangle^* + \langle r'|2s\rangle^* \langle r''|1s\rangle^*] H_1(r',r'')$$

$$[\langle r'|1s\rangle \langle r''|2s\rangle - \langle r'|2s\rangle \langle r''|1s\rangle]$$

$$= \frac{V_{11} - V_{12} + V_{21} - V_{22}}{2}$$

$$= \frac{-K + K^*}{2}$$

$$\langle\psi_-|\hat{H}_1|\psi_+\rangle = \iint d^3r' d^3r'' \psi_-^*(r',r'')H_1(r',r'')\psi_+(r',r'')$$

$$= \frac{1}{2}\iint[\langle r'|1s\rangle^*\langle r''|2s\rangle^* - \langle r'|2s\rangle^*\langle r''|1s\rangle^*]H_1(r',r'')$$

$$[\langle r'|1s\rangle\langle r''|2s\rangle + \langle r'|2s\rangle\langle r''|1s\rangle]$$

$$= \frac{V_{11} + V_{12} - V_{21} - V_{22}}{2}$$

$$= \frac{K - K^*}{2}$$

$$\langle\psi_-|\hat{H}_1|\psi_-\rangle = \iint d^3r' d^3r'' \psi_-^*(r',r'')H_1(r',r'')\psi_-(r',r'')$$

$$= \frac{1}{2}\iint d^3r' d^3r''[\langle r'|1s\rangle^*\langle r''|2s\rangle^* - \langle r'|2s\rangle^*\langle r''|1s\rangle^*]H_1(r',r'')$$

$$[\langle r'|1s\rangle\langle r''|2s\rangle - \langle r'|2s\rangle\langle r''|1s\rangle]$$

$$= \frac{V_{11} - V_{12} - V_{21} + V_{22}}{2}$$

$$= J - \frac{K + K^*}{2}$$

where

$$V_{11} = \iint d^3r' d^3r'' \langle r'|1s\rangle^*\langle r''|2s\rangle^* H_1(r',r'')\langle r'|1s\rangle\langle r''|2s\rangle$$

$$= \iint d^3r' d^3r'' |\langle r'|1s\rangle|^2 |\langle r''|2s\rangle|^2 H_1(r',r'')$$

$$V_{12} = \iint d^3r' d^3r'' \langle r'|1s\rangle^*\langle r''|2s\rangle^* H_1(r',r'')\langle r'|2s\rangle\langle r''|1s\rangle]$$

$$V_{21} = \iint d^3r' d^3r'' \langle r'|2s\rangle^*\langle r''|1s\rangle^* H_1(r',r'')\langle r'|1s\rangle\langle r''|2s\rangle$$

$$V_{22} = \iint d^3r' d^3r'' \langle r'|2s\rangle^*\langle r''|1s\rangle^*]H_1(r',r'')\langle r'|2s\rangle\langle r''|1s\rangle$$

$$= \iint d^3r' d^3r'' |\langle r'|2s\rangle|^2 |\langle r''|1s\rangle|^2 H_1(r',r'')$$

When K is real, we have the matrix of H_1 under the basis of $\{|\psi_+\rangle, |\psi_-\rangle\}$;

$$H_1 = \begin{pmatrix} J + K & 0 \\ 0 & J - K \end{pmatrix},$$

where

$$V_{11} = V_{22} = J = \frac{17e^2}{81a_0} Z = \frac{17}{81} Z (2 \times \frac{1}{2} m_e c^2 \alpha^2) = 11.42 \text{ eV},$$

$$V_{12} = V_{21} = K = \frac{16e^2}{729a_0} Z = \frac{16}{729} Z (2 \times \frac{1}{2} m_e c^2 \alpha^2) = 1.19 \text{ eV},$$

with

$$\frac{e^2}{a_0} = m_e c^2 \alpha^2 = 2 \times \frac{1}{2} m_e c^2 \alpha^2 = 2R = 27.2 eV .$$

This implies that

$$\hat{H}_1 |\psi_+\rangle = (J + K)|\psi_+\rangle , \qquad \hat{H}_1 |\psi_-\rangle = (J - K)|\psi_-\rangle .$$

For $|\psi_+\rangle = |\psi_s\rangle$ the first-order energy correction is given by

$$E_1^{(1)} = J + K \qquad \text{for} \qquad S = 0 \text{ (singlet).}$$

For $|\psi_-\rangle = |\psi_a\rangle$ the first-order energy correction is given by

$$E_1^{(1)} = J - K \qquad \text{for} \qquad S = 1 \text{ (triplet).}$$

9. Heisenberg's ferromagnet model

Here we introduce an effective spin Hamiltonian:

$$\hbar^2 S(S+1) = \hat{S}^2 = (\hat{S}_1 + \hat{S}_2)^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2\hat{S}_1 \cdot \hat{S}_2 = \frac{3}{2}\hbar^2 + 2\hat{S}_1 \cdot \hat{S}_2 ,$$

or

$$\frac{1}{\hbar^2} 2\hat{S}_1 \cdot \hat{S}_2 = S(S+1) - \frac{3}{2} .$$

When $S = 1$ (triplet),

$$\frac{1}{\hbar^2} 2\hat{S}_1 \cdot \hat{S}_2 = \frac{1}{2} , \qquad (\hat{\sigma}_1 \cdot \hat{\sigma}_2 = 1),$$

or

$$\hat{P}_{12} = \frac{1}{2}(\hat{1} + \hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2) \rightarrow 1.$$

When $S = 0$ (singlet),

$$\frac{1}{\hbar^2} 2\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2 = -\frac{3}{2}, \qquad (\hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2 = -3),$$

or

$$\hat{P}_{12} = \frac{1}{2}(\hat{1} + \hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2) \rightarrow -1.$$

Then the effective spin Hamiltonian can be rewritten as

$$\begin{aligned}
\left(\hat{H}_1\right)_{eff} &= J\hat{1} - \frac{1}{2}K(\hat{1} + \hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2) \\
&= (J - \frac{1}{2}K)\hat{1} - \frac{1}{2}K\hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2 \quad . \\
&= (J - \frac{1}{2}K)\hat{1} - K\frac{2}{\hbar^2}\hat{\boldsymbol{S}}_1 \cdot \hat{\boldsymbol{S}}_2
\end{aligned}$$

When K is positive, we say that the interaction between spins is ferromagnetic. If K is negative, the interaction is antiferromagnetic. This Hamiltonian is called the **Heisenberg model**, which was first proposed by Heisenberg.

((Note))

We note that $\left(H_1\right)_{eff}$ is expressed by

$$\begin{aligned}
(H_1)_{eff} &= (J - \frac{1}{2}K)\hat{1} - \frac{1}{2}K\hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2 \\
&= (J - \frac{1}{2}K)\hat{1}_2 \otimes \hat{1}_2 - \frac{1}{2}K(\hat{\sigma}_{1x} \otimes \hat{\sigma}_{2x} + \hat{\sigma}_{1y} \otimes \hat{\sigma}_{2y} + \hat{\sigma}_{1z} \otimes \hat{\sigma}_{2z}) \\
&= \begin{pmatrix} J - K & 0 & 0 & 0 \\ 0 & J & -K & 0 \\ 0 & -K & J & 0 \\ 0 & 0 & 0 & J - K \end{pmatrix}
\end{aligned}$$

under the basis of $|++\rangle, |+-\rangle, |-+\rangle, |--\rangle$ }. We can solve the eigenvalue problem for $(H_1)_{eff}$. Of course we have the eigenvalues,

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$(J - K)$ for $S = 1$ state and $(J + K)$ for $S = 0$ state.

Eigenvalue: $(J - K)$ Eigenstate : $\left|++\right\rangle, \dfrac{1}{\sqrt{2}}(\left|+-\right\rangle+\left|-+\right\rangle), \left|--\right\rangle$

Eigenvalue: $(J + K)$ Eigenstate: $\dfrac{1}{\sqrt{2}}(\left|+-\right\rangle-\left|-+\right\rangle)$

((**Note**))   Dirac exchange operator

$$\left(\hat{H}_1\right)_{eff} = J\hat{1} - K\hat{P}_{12}$$

where

$$\hat{P}_{12} = \frac{1}{2}(\hat{1} + \hat{\sigma}_1 \cdot \hat{\sigma}_2)$$

Thus we have

$$\left(\hat{H}_1\right)_{eff}\left|++\right\rangle = (J\hat{1} - K\hat{P}_{12})\left|++\right\rangle = (J - K)\left|++\right\rangle$$

$$\left(\hat{H}_1\right)_{eff}\left|--\right\rangle = (J\hat{1} - K\hat{P}_{12})\left|--\right\rangle = (J - K)\left|--\right\rangle$$

$$\left(\hat{H}_1\right)_{eff}\left|+-\right\rangle = (J\hat{1} - K\hat{P}_{12})\left|+-\right\rangle = J\left|+-\right\rangle - K\left|-+\right\rangle$$

$$\left(\hat{H}_1\right)_{eff}\left|-+\right\rangle = (J\hat{1} - K\hat{P}_{12})\left|-+\right\rangle = J\left|-+\right\rangle - K\left|+-\right\rangle$$

((**Note**))
The excited state thus obtained are characterized by L, S, and J as follows.

(1)	$L = 0$,	$S = 1$,	$J = 1$	$^3S_1$
(2)	$L = 0$,	$S = 0$	$J = 0$	$^1S_0$
(3)	$L = 1$,	$S = 1$,	$J = 2, 1, 0$	$^3P_2, {}^3P_1, {}^3P_0$
(4)	$L = 1$,	$S = 0$,	$J = 1$	$^1P_1$

where J is the total angular momentum, L is the orbital angular momentum, S is the total angular momentum of the system.

((**Mathematica**)) Solving the eigenvalue problem of $(H_1)_{eff}$;

```
Clear["Global`*"]; S = 1 / 2; ℏ = 1;
exp_* :=
  exp /. {Complex[re_, im_] :> Complex[re, -im]};

σx = PauliMatrix[1]; σy = PauliMatrix[2];
σz = PauliMatrix[3]; I2 = IdentityMatrix[2];
I4 = IdentityMatrix[4];

H1 =
  J I4 -
    1
    ─ K (KroneckerProduct[I2, I2] +
    2
      KroneckerProduct[σx, σx] +
      KroneckerProduct[σy, σy] +
      KroneckerProduct[σz, σz]) // Simplify;

H1 // MatrixForm
```

$$
\begin{pmatrix}
J - K & 0 & 0 & 0 \\
0 & J & -K & 0 \\
0 & -K & J & 0 \\
0 & 0 & 0 & J - K
\end{pmatrix}
$$

```
eq1 = Eigensystem[H1]
```

```
{{J - K, J - K, J - K, J + K}, {{0, 0, 0, 1},
  {0, 1, 1, 0}, {1, 0, 0, 0}, {0, -1, 1, 0}}}
```

---

10.   Evaluation of *J* and *K*
((Mathematica))

$$
\psi_{1s}(r) = \langle r|1s \rangle = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-\frac{Zr}{a_0}},
$$

$$
\langle r|2s \rangle = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-\frac{Zr}{2a_0}} (2 - \frac{Zr}{a_0}),
$$

$$
H_1(r',r") = \frac{e^2}{|r'-r"|},
$$

$$
V_{11} = \iint d^3r' d^3r" \langle r'|1s \rangle^* \langle r"|2s \rangle^* H_1(r',r") \langle r'|1s \rangle \langle r"|2s \rangle
$$
$$
= \iint d^3r' d^3r" |\langle r'|1s \rangle|^2 |\langle r"|2s \rangle|^2 H_1(r',r")
$$
$$
= \frac{17e^2}{81a_0} Z
$$

$$V_{12} = \iint d^3r' \, d^3r'' \langle r'|1s\rangle^* \langle r''|2s\rangle^* H_1(r',r'') \langle r'|2s\rangle \langle r''|1s\rangle]$$

$$= \int_0^\infty 4\pi r_1^2 \langle r_1|1s\rangle^* \langle r_1|2s\rangle dr_1 \int_0^\infty r_2^2 \langle r_2|1s\rangle \langle r_2|2s\rangle^* dr_2 \int_0^\pi 2\pi \sin\theta \frac{e^2}{|r_1-r_2|} d\theta$$

$$= \frac{16e^2}{729a_0} Z$$

$$V_{22} = \iint d^3r_1 \, d^3r_2 |\langle r_1|2s\rangle|^2 |\langle r_2|1s\rangle|^2 H_1(r_1,r_2)$$

$$= \int_0^\infty 4\pi r_1^2 |\langle r_1|2s\rangle|^2 dr_1 \int_0^\infty |\langle r_2|1s\rangle|^2 r_2^2 dr_2 \int_0^\pi 2\pi \sin\theta \frac{e^2}{|r_1-r_2|} d\theta$$

$$= \frac{17e^2}{81a_0} Z$$

11. Mathematica
(a)   Calculation of V_{12}

```
Clear["Global`*"]; ψ[n_, ℓ_, m_, r_, θ_, ϕ_] :=
  1/ (√ (n + ℓ) !)

  (2^(1+ℓ) a^(-ℓ-3/2) e^(-Z1 r/(a n)) n^(-ℓ-2) Z1^(ℓ+3/2) r^ℓ √ (n - ℓ - 1) !

    LaguerreL[-1 + n - ℓ, 1 + 2 ℓ, (2 Z1 r) / (a n)])

  SphericalHarmonicY[ℓ, m, θ, ϕ];
ψ1s[r_] := ψ[1, 0, 0, r, θ, ϕ];

ψ2s[r_] := ψ[2, 0, 0, r, θ, ϕ];
             e1²
f1 = ──────────────────────────── ;
     √ r1² + r2² - 2 r1 r2 Cos[θ]

eq1 = Integrate[2 π Sin[θ] f1, {θ, 0, π}] //
   Simplify[#, {r1 > 0, r2 > 0, (r1 - r2)² > 0}] &;
f11 = eq1 // Simplify[#, r2 < r1] &; f12 = eq1 // Simplify[#, r2 > r1] &;
g11 = r2² ψ1s[r2] ψ2s[r2] f11 ; g12 = r2² ψ1s[r2] ψ2s[r2] f12 ;
a1 = Integrate[g11, {r2, 0, r1}] // FullSimplify;

a2 = Integrate[g12, {r2, r1, ∞}] // FullSimplify[#, Re[Z1/a] > 0] &;

a12 = (a1 + a2) // Simplify; a3 = a12 4 π r1² ψ1s[r1] ψ2s[r1] ;

Integrate[a3, {r1, 0, ∞}] // FullSimplify[#, Re[Z1/a] > 0] &

16 e1² Z1
──────────
  729 a
```

(b)   Calculation of V_{11}

```mathematica
Clear["Global`*"]; ψ[n_, ℓ_, m_, r_, θ_, ϕ_] :=
 1/(√((n + ℓ)!)
  (2^(1+ℓ) a^(-ℓ-3/2) e^(-(Z1 r)/(a n)) n^(-ℓ-2) Z1^(ℓ+3/2) r^ℓ √((n - ℓ - 1)!)

    LaguerreL[-1 + n - ℓ, 1 + 2 ℓ, (2 Z1 r)/(a n)])

   SphericalHarmonicY[ℓ, m, θ, ϕ];
ψ1s[r_] := ψ[1, 0, 0, r, θ, ϕ];

ψ2s[r_] := ψ[2, 0, 0, r, θ, ϕ];

f1 = (e1^2)/(√(r1^2 + r2^2 - 2 r1 r2 Cos[θ]));

eq1 = Integrate[2 π Sin[θ] f1, {θ, 0, π}] //
   Simplify[#, {r1 > 0, r2 > 0, (r1 - r2)^2 > 0}] &;
f11 = eq1 // Simplify[#, r2 < r1] &; f12 = eq1 // Simplify[#, r2 > r1] &;
g11 = r2^2 ψ1s[r2]^2 f11; g12 = r2^2 ψ1s[r2]^2 f12;
a1 = Integrate[g11, {r2, 0, r1}] // FullSimplify;

a2 = Integrate[g12, {r2, r1, ∞}] // FullSimplify[#, Re[Z1/a] > 0] &;

a12 = (a1 + a2) // Simplify; a3 = a12 4 π r1^2 ψ2s[r1]^2;

Integrate[a3, {r1, 0, ∞}] // FullSimplify[#, Re[Z1/a] > 0] &
```

$$\frac{17\, e1^2\, Z1}{81\, a}$$

12.   Summary

Orthohelium:

For spin triplet (symmetric spin part), we have an anti-symmetric space part $\left|\psi_{space}^{(a)}\right\rangle$ with energy I - J.

$$E_1^{(0)} = E(1,0,0) + E(n,l,m),$$

$$E_1^{(1)} = I - J.$$

Parahelium:

For spin singlet (antisymmetric), we have a symmetrical space part $\left|\psi_{space}^{(s)}\right\rangle$ with energy I + J.

$$E_1^{(0)} = E(1,0,0) + E(n,l,m)$$
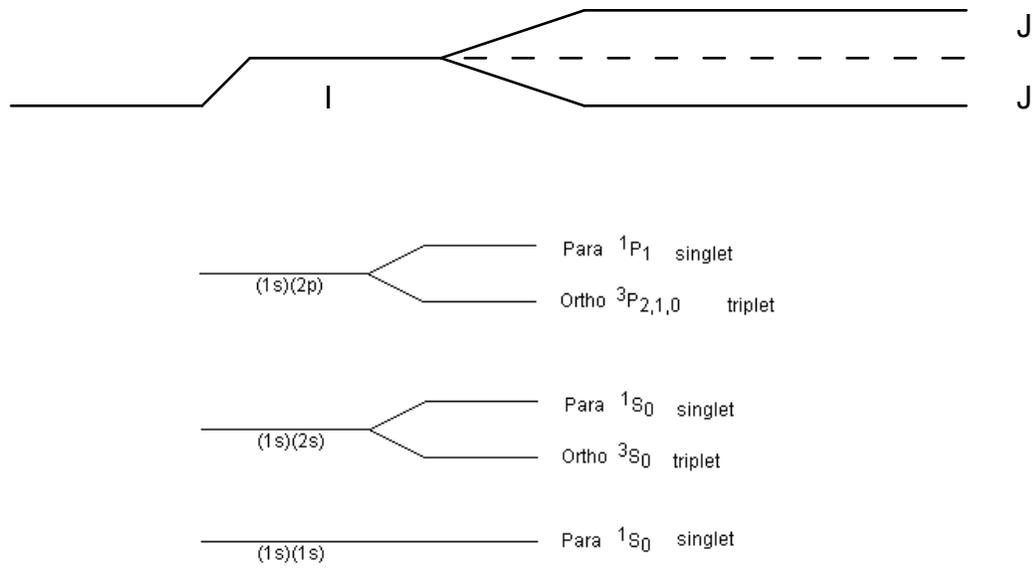
$$E_1^{(1)} = I + J$$

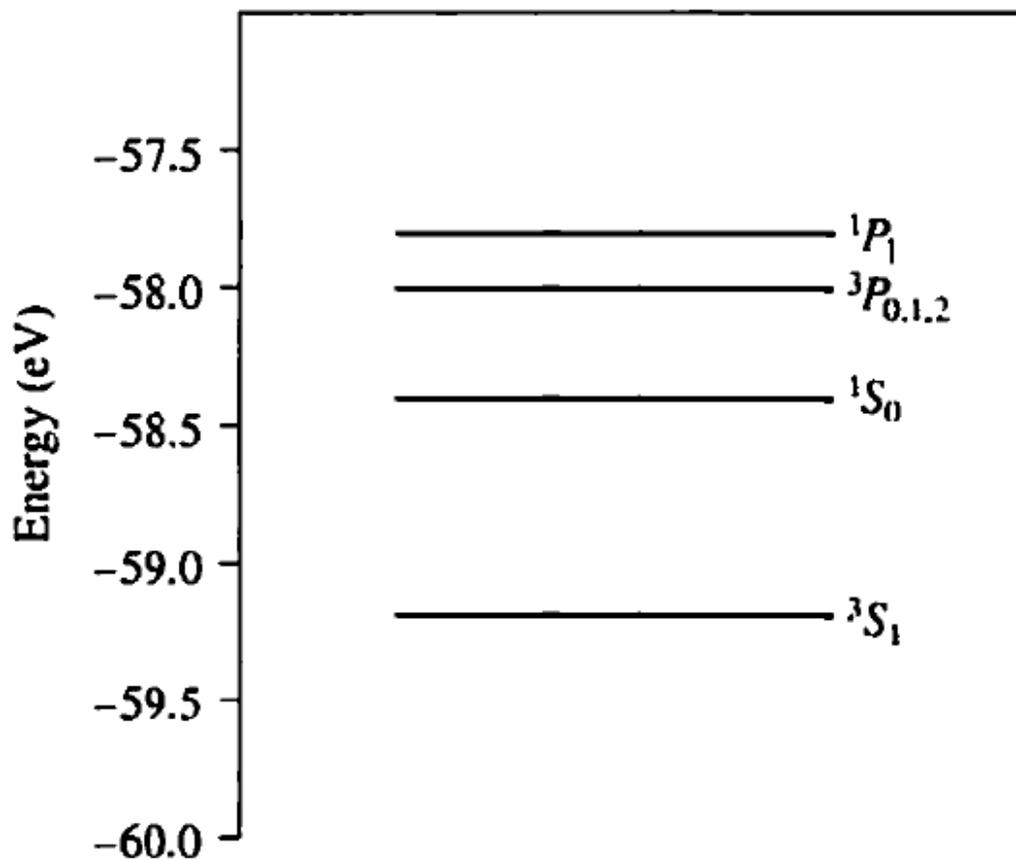Fig.   Schematic energy level diagram for low-lying configurations of He atom.

Fig. An energy-level diagram of the first excited states of He (Townsend, Quantum Physics)

13. Orthohelium and parahelium

In the helium energy level diagram, one electron is presumed to be in the ground state of a helium atom, the 1s state. An electron in an upper state can have spin antiparallel to the ground state electron ($S=0$, singlet state, parahelium) or parallel to the ground state electron ($S=1$, triplet state, orthohelium).

It is observed that the orthohelium states are lower in energy than the parahelium states. The explanation for this is:

1. The parallel spins make the spin part of the wavefunction symmetric.
2. The total wavefunction for the electrons must be anti-symmetric since they are fermions and must obey the Pauli exclusion principle.
3. This forces the space part of the wavefunction to be anti-symmetric. The wavefunction for the electrons can be written as the product of the space and spin parts of the wavefunction.

4. An anti-symmetric space wavefunction for the two electrons implies a larger average distance between them than a symmetric function of the same type. The probability is the square of the wavefunction, and from a simple functional point of view, the square of an antisymmetric function must go to zero at the origin. So in general, the probability for small separations of the two electrons is smaller than for a symmetric space wavefunction.
5. If the electrons are on the average further apart, then there will be less shielding of the nucleus by the ground state electron, and the excited state electron will therefore be more exposed to the nucleus. This implies that it will be more tightly bound and of lower energy.

This effect is sometimes called the "spin-spin interaction" and is addressed by Hund's Rule . It is part of the understanding of the ordering of energy levels in multi-electron atoms.

14. A simpler approach to the Heisenberg's model on ferromagnetism
(a) Comment on the commutation relation
For the sake of clarity, here we use the perturbation Hamiltonian as

$$\hat{V} = \frac{e^2}{|\hat{r}_1 - \hat{r}_2|}$$

We have the following commutation relations,

$$[\hat{V}, \hat{L}^2] = 0, \quad [\hat{V}, \hat{L}_z] = 0$$

$$[\hat{H}_0, \hat{L}^2] = 0, \quad [\hat{H}_0, \hat{L}_z] = 0$$

$$[\hat{H}, \hat{L}^2] = 0, \quad [\hat{H}, \hat{L}_z] = 0$$

where

$$\hat{H} = \hat{H}_0 + \hat{V}. \quad \hat{L} = \hat{L}_1 + \hat{L}_2$$

$\hat{L}$ is the total orbital angular momentum.

((**Merzbacher**))
The unperturbed energy levels are degenerate exactly as in the hydrogen atom, but the interaction between the two electrons removes the *l*-degeneracy. The unperturbed

eigenfunctions of $|100\rangle = |1s\rangle$ and $|nlm\rangle$ are used as the unperturbed eigenfunctions for the degenerate perturbation treatment. Due to the perturbation potential, the resulting eigenfunctions are the combination of $|100\rangle = |1s\rangle$ and $|nlm\rangle$, forming the symmetric state and the antisymmetric state. Note that the total angular momentum is conserved. Two different exchange symmetry cannot mix.

$$\hat{L}_{z1}|100\rangle_1|nlm\rangle_2 = 0\hbar|100\rangle_1|nlm\rangle_2 = 0$$

$$\hat{L}_{z2}|100\rangle_1|nlm\rangle_2 = m\hbar|100\rangle_1|nlm\rangle_2$$

$$\hat{L}_z|100\rangle_1|nlm\rangle_2 = (\hat{L}_{z1} + \hat{L}_{z2})|100\rangle_1|nlm\rangle_2 = m\hbar|100\rangle_1|nlm\rangle_2$$

Similarly

$$\hat{L}_z|nlm\rangle_1|100\rangle_2 = (\hat{L}_{z1} + \hat{L}_{z2})|nlm\rangle_1|100\rangle_2 = m\hbar|nlm\rangle_1|100\rangle_2$$

(ii)

$$\hat{L}^2 = (\hat{L}_1 + \hat{L}_2)^2 = \hat{L}_1^2 + \hat{L}_2^2 + 2\hat{L}_{1z}\hat{L}_{2z} + (\hat{L}_{1+}\hat{L}_{2-} + \hat{L}_{1-}\hat{L}_{2+})$$

Noting the formula given by

$$\hat{L}_+|nl,m\rangle = \hbar\sqrt{(l-m)(l+m+1)}|nl,m+1\rangle$$

$$\hat{L}_-|nl,m\rangle = \hbar\sqrt{(l+m)(l-m+1)}|nl,m-1\rangle$$

we have

$$\hat{L}_{2+}|100\rangle_1|nlm\rangle_2 = \hbar\sqrt{(l-m)(l+m+1)}|100\rangle_1|nl,m+1\rangle_2$$

$$\hat{L}_{1-}\hat{L}_{2+}|100\rangle_1|nlm\rangle_2 = \hbar\sqrt{(l-m)(l+m+1)}\hat{L}_{1-}|100\rangle_1|nl,m+1\rangle_2 = 0$$

$$\hat{L}_{2-}|100\rangle_1|nlm\rangle_2 = \hbar\sqrt{(l+m)(l-m+1)}|100\rangle_1|nl,m-1\rangle_2$$

$$\hat{L}_{1+}\hat{L}_{2-}|100\rangle_1|nlm\rangle_2 = \hbar\sqrt{(l+m)(l-m+1)}\hat{L}_{1+}|100\rangle_1|nl,m-1\rangle_2 = 0$$

leading to

$$\hat{L}^2|100\rangle_1|nlm\rangle_2 = [\hat{L}_1^2 + \hat{L}_2 + 2\hat{L}_{1z}\hat{L}_{2z} + (\hat{L}_{1+}\hat{L}_{2-} + \hat{L}_{1-}\hat{L}_{2+})]|100\rangle_1|nlm\rangle_2$$
$$= \hbar^2 l(l+1)|100\rangle_1|nlm\rangle_2$$

Similarly

$$\hat{L}^2|nlm\rangle_1|100\rangle_2 = [\hat{L}_1^2 + \hat{L}_2 + 2\hat{L}_{1z}\hat{L}_{2z} + (\hat{L}_{1+}\hat{L}_{2-} + \hat{L}_{1-}\hat{L}_{2+})]|nlm\rangle_1|100\rangle_2$$
$$= \hbar^2 l(l+1)|nlm\rangle_1|100\rangle_2$$

Both $|100\rangle_1|nlm\rangle_2$ and $|nlm\rangle_1|100\rangle_2$ are the eigenkets of $\hat{L}^2$ and $\hat{L}_z$ with the eigenvalues $\hbar^2 l(l+1)$ and $\hbar m$, respectively.

(b)   Selection rule

We use the commutation relations;

$$[\hat{V}, \hat{L}_z] = 0, \quad [\hat{V}, \hat{L}^2] = 0$$

$$\hat{L}_z \hat{V}|100\rangle_1|nlm\rangle_2 = \hat{V}\hat{L}_z|100\rangle_1|nlm\rangle_2 = m\hbar\hat{V}|100\rangle_1|nlm\rangle_2$$

$$\hat{L}^2 \hat{V}|100\rangle_1|nlm\rangle_2 \hat{V}\hat{L}^2|100\rangle_1|nlm\rangle_2 = \hbar^2 l(l+1)\hat{V}|100\rangle_1|nlm\rangle_2$$

Both $\hat{V}|100\rangle_1|nlm\rangle_2$ and $\hat{V}|nlm\rangle_1|100\rangle_2$ are the eigenket of $\hat{L}^2$ and $\hat{L}_z$ with the eigenvalues $\hbar^2 l(l+1)$ and $\hbar m$, respectively.

(c)   Permutation operator

$$\hat{V} = \frac{e^2}{|\hat{r}_1 - \hat{r}_2|}$$

$$\hat{P}_{12}\hat{V}\hat{P}_{12}^{-1} = \hat{P}_{12}\hat{V}\hat{P}_{12} = \hat{V}$$

$$\hat{P}_{12}^2 = \hat{1}, \qquad \hat{P}_{12}^+ = \hat{P}_{12} = \hat{P}_{12}^{-1}$$

We now consider the matrix of the perturbation Hamiltonian $\hat{V}$ under the basis of $\{|1s, 2s\rangle, |2s, 1s\rangle\}$;

$$|1s, 2s\rangle = |1s\rangle_1 |2s\rangle_2, \quad |2s, 1s\rangle = |2s\rangle_1 |1s\rangle_2$$

Note that

$$\hat{P}_{12}|1s, 2s\rangle = \hat{P}_{12}|1s\rangle_1 |2s\rangle_2 = |2s\rangle_1 |1s\rangle_2$$

$$\langle 2s|_1 \langle 1s|_2 = \langle 1s|\langle 2s|\hat{P}_{12}^+ = \langle 1s|\langle 2s|\hat{P}_{12}$$

We define the matrix elements

$$J = \langle 1s, 2s|\hat{V}|1s, 2s\rangle$$

$$K = \langle 1s, 2s|\hat{V}|2s, 1s\rangle$$
$$= \langle 1s, 2s|\hat{V}|2s, 1s\rangle$$
$$= \langle 1s, 2s|\hat{V}\hat{P}_{12}|1s, 2s\rangle$$
$$= \langle 1s, 2s|\hat{V}|2s, 1s\rangle$$

$$\langle 2s, 1s|\hat{V}|1s, 2s\rangle = \langle 1s, 2s|\hat{P}_{12}\hat{V}|1s, 2s\rangle$$
$$= \langle 1s, 2s|\hat{V}\hat{P}_{12}|1s, 2s\rangle$$
$$= \langle 1s, 2s|\hat{V}|2s, 1s\rangle$$
$$= K$$

$$\langle 2s, 1s|\hat{V}|2s, 1s\rangle = \langle 1s, 2s|\hat{P}_{12}\hat{V}\hat{P}_{12}|1s, 2s\rangle = \langle 1s, 2s|\hat{V}|1s, 2s\rangle = J$$

Then we have the matrix of $\hat{V}$ under the basis of $\{|1s, 2s\rangle, |2s, 1s\rangle\}$ as

$$\hat{V} = \begin{pmatrix} J & K \\ K & J \end{pmatrix} = J\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + K\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = J\hat{1} + K\hat{\sigma}_x$$

The eigenvalue problem:

$$\hat{V}|+x\rangle = (J\hat{1} + K\hat{\sigma}_x)|+x\rangle = (J+K)|+x\rangle$$

where

$$|+x\rangle = \frac{1}{\sqrt{2}}[|1s, 2s\rangle + |2s, 1s\rangle]$$ (symmetric orbital state; antisymmetric spin state)

with the eigenvalue $J + K$

$$\hat{V}|-x\rangle = (J\hat{1} + K\hat{\sigma}_x)|-x\rangle = (J-K)|+x\rangle$$

where

$$|-x\rangle = \frac{1}{\sqrt{2}}[|1s, 2s\rangle - |2s, 1s\rangle]$$ (antisymmetric orbital state; symmetric spin state)

with the eigenvalue $J - K$

We note that the permutation operator is expressed by

$$\hat{P}_{12} = \frac{1}{2}(1 + \hat{\sigma}_1 \cdot \hat{\sigma}_2)$$

$$\hat{P}_{12}|\chi_s\rangle = |\chi_s\rangle, \qquad \hat{P}_{12}|\chi_a\rangle = -|\chi_a\rangle$$

where

$$|\chi_s\rangle = \frac{1}{\sqrt{2}}[|+,-\rangle + |-,+\rangle]$$ (corresponding to $\frac{1}{\sqrt{2}}[|1s, 2s\rangle - |2s, 1s\rangle]$)

$$|\chi_a\rangle = \frac{1}{\sqrt{2}}[|+,-\rangle - |-,+\rangle]$$ (corresponding to $\frac{1}{\sqrt{2}}[|1s, 2s\rangle + |2s, 1s\rangle]$)

Then we have a spin Hamiltonian defined by

$$\hat{V} = J\hat{1} - K\,\hat{P}_{12}$$

$$= J\hat{1} - \frac{K}{2}(\hat{1} + \hat{\sigma}_1 \cdot \hat{\sigma}_2)$$

$$= (J - \frac{K}{2})\hat{1} - \frac{2K}{\hbar^2}\hat{S}_1 \cdot \hat{S}_2$$

leading to the Heisenberg's exchange interaction between spins.

((**Note**))
The spin Hamiltonian of the Heisenberg model is expressed in the form

$$\hat{H} = -2J \sum_{<i,j>} \hat{S}_i \cdot \hat{S}_j$$

where the sum is over the nearest neighbor pairs of atoms. J is the exchange integral (units of energy) and is related to the overlap of the charge distributions of atoms i and j. $\hat{S}_i$ is the spin operator (dimensionless).

15.   Origin of ferromagnetism: Weiss model
The exchange field gives an approximate representation of the quantum-mechanical exchange interaction

$$E_{ex} = -2J \sum_{<i,j>} S_i \cdot S_j \,, \tag{28}$$

where the sum is over nearest neighbor pairs. J is the exchange interaction and is related to the overlap of the charge distribution of spins i, j. This equation is called the Heisenberg model. The interaction related to the i-th spin is given by

$$E_{ex} \mid = -2Jz < S > \cdot S_i = -(-g\mu_B S_i) \cdot B(i) \,, \tag{29}$$

where z is the number of nearest-neighbor spins and $B(i)$ is the exchange field seen by the i-th spin,
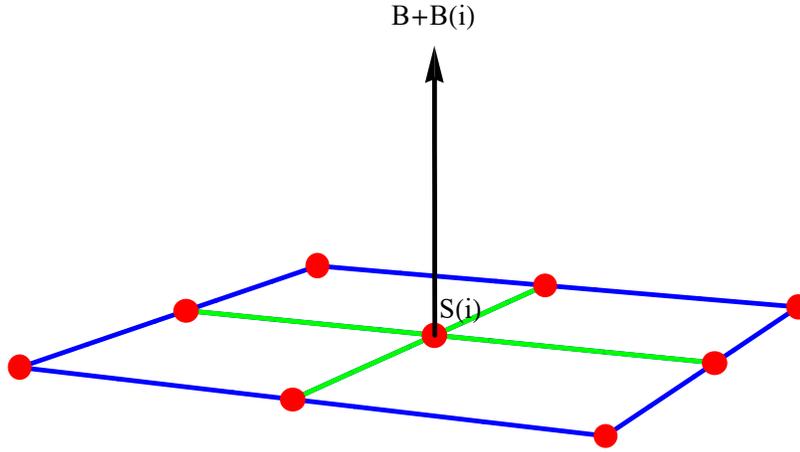
$$B(i) = -\frac{2Jz}{g\mu_B} < S > .$$

Fig. Mean field $B(i)$ applied the spin S_i (at the center in this Fig), arising from the exchange interaction with the surrounding spins (in this case, $z = 4$). B is the applied magnetic field.

The magnetization M is given by

$$\mathbf{M} = -g\mu_B N_A < \mathbf{S} > .$$

Then the exchange field is

$$\mathbf{B}(i) = -\frac{2Jz}{g\mu_B} \frac{\mathbf{M}}{(-g\mu_B N_A)} = \frac{2zJ}{g^2\mu_B^2 N_A} \mathbf{M} = A\mathbf{M} ,$$

which means that

$$A = \frac{2zJ}{g^2\mu_B^2 N_A} .$$

In the presence of a mean field, the molar magnetization can be described by

$$M = \frac{C_M}{T}[B + AM]$$

where C_M is the Curie constant and is given by

$$C_M = \frac{N_A g^2 \mu_B^2 S(S+1)}{3k_B}$$

From this equation M can be derived as

$$M = \frac{C_M}{T - CA} B$$

The corresponding susceptibility is

$$\chi_M = \frac{M}{B} = \frac{C_M}{T - C_M A} = \frac{C_M}{T - \Theta} \qquad \text{(Curie-Weiss law)}$$

The Curie-Weiss temperature Θ is given by

$$\Theta = C_M A = \frac{N_A g^2 \mu_B^2 S(S+1)}{3k_B} \frac{2zJ}{g^2 \mu_B^2 N_A} = \frac{2zJ}{3k_B} S(S+1).$$

where the Curie-Weiss constant is defined by

$$C_M = \frac{N_A g^2 \mu_B^2 S(S+1)}{3k_B}$$

Note that Θ is positive for ferromagnetic exchange interaction ($J > 0$) and Θ is negative for antiferromagnetic interaction ($J > 0$). From this equation J is expressed in terms of Θ as

$$J = \frac{3k_B \Theta}{2zS(S+1)}.$$

From this expression, one can evaluate the value of exchange interaction between the nearest neighbor interactions.

((Example))   C. Kittel Introduction to Solid State Physics

For Fe, $\Theta = 1043K$. $g = 2$ (Landé g-factor). S = 1.

$$B_E \approx 10^7 \, \text{G} = 10^3 \, \text{T.} \quad J = 11.9 \text{ meV.}$$

16.   Origin of ferromagnetism (Heisenberg: 1926-1928)
L. Hoddeson et al, edited, Out of the Crystal Maze: Chapters from the History of Solid-State Physics (Oxford, 1992).

Heisenberg's article closely followed the lines of his correspondence with Pauli in both 1926 and 1928. After noting that neglect of electron interactions leads, according to Pauli, to paramagnetism or diamagnetism, he described the basis of his theory: "The empirical phenomenon that ferromagnetism presents is very similar to the situation we

met earlier in the case of the helium atom." The clue was the splitting of the two-electron helium atom into singlet and triplet terms by the exchange interaction. He continued, "We will try to show that the Coulomb interaction together with the Pauli principle suffice to give the same result as the molecular field postulated by Weiss. Only very recently have the mathematical methods for treating such a complicated problem been developed by Wigner, Hund, Heitler and London." Recalling the Heitler-London expression for the exchange integral, and explaining how the exchange energy can tend to align spins, he then launched into a very formal calculation of the energy levels in terms of the characters of the permutation group, finally specializing to nearest neighbor interactions with a common exchange integral and introducing the Gaussian approximation. His resulting version of the Weiss formula implied that a spin must have at least eight nearest neighbors for the system to become ferromagnetic, a result he continued to regard as significant; it also implies that the system must become paramagnetic again at low temperature, but he did not "believe that this result has physical meaning. It arises mathematically through the assumed Gaussian distribution of the energy values."

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APPEDIX-I   Origin of ferromagnetism (Tomonaga's comment)

"The effect of the apparently large interaction between electron spins is not limited to spectral term values. In order to explain the ferromagnetism of Fe, as you may know, P. Weiss proposed long ago that there is a large interaction between molecular magnets based on the then-accepted concept of the molecular magnet. By using this idea, Weiss could explain a wide variety of experimental results related to ferromagnetism. However, the origin of such a strong interaction between molecular magnets was entirely unknown.

Then there appeared the new interpretation of the spectral terms of alkaline earths. This new interpretation was given by Heisenberg in 1926; he not only discovered that the symmetry properties of the wave function has a close connection to a particle's statistics in a many-electron system but also found that it plays an important role in a variety of problems and for the first time gave a clear explanation of the spectral terms of two-electron systems. Furthermore, immediately after this work he applied the same idea to the problem of ferromagnetism."

[S. Tomonaga, The Story of Spins (University of Chicago Press, 1997). The original book (in Japanese) was published from Chuokoron-sha (1974). It was translated from Japanese to English by Prof. Takeshi Oka].

APPENDIX-II   Origin of ferromagnetism (Wannier's comment)

The discovery of the correct nature for the ferromagnetic coupling force came as a by-product of quantum mechanics. Dirac showed that the electronic spin and the Pauli exclusion principle combine in such a way as to produce between the spins of two neighboring electrons a coupling of the form $J\hat{\boldsymbol{\sigma}}_1 \cdot \hat{\boldsymbol{\sigma}}_2$. Here $\hat{\boldsymbol{\sigma}}_1$ and $\hat{\boldsymbol{\sigma}}_2$ are the two spins and J is a function of distance called the exchange energy or exchange coupling. It can be of either sign. If the wave functions of the two electrons interpenetrate substantially the exchange energy is of the same order as the electrostatic interaction, but at larger distances it falls exponentially as the wave functions themselves. We may therefore think of J as being of electrostatic order, but only acting between close neighbors. Heisenberg was the first to realize that this exchange energy J, if of negative sign, offers a natural explanation for the phenomenon of ferromagnetism.

[G.H. Wannier, Elements of Solid State Theory (Cambridge, 1960)].

APPENDIX –III   Heisenberg (1963)

M. Longair, Quantum Concepts in Physics (Cambridge, 2013).

'For a long time, I continued to mix up Bose–Einstein and Fermi–Dirac statistics. I did not know Fermi–Dirac statistics at that time; I knew only the Pauli exclusion principle. I was always confused between Bose–Einstein statistics and the Pauli exclusion principle which produce different ways of counting states. When I wrote the equations for two identical electrons, there were two solutions, one symmetrical and the other anti-symmetrical. First I thought that I had to take the anti-symmetrical solution to obtain the Bose statistics and that must be the one that gave the Pauli principle. Later, I saw that it was the other way around. One must take the symmetrical solution to get Bose statistics, and the antisymmetrical solution to get Pauli's exclusion principle.' (Heisenberg, 1963).